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PREPARATION AND CHARACTERIZATION OF SEVERAL  
CONDUCTION TRANSITION METAL OXIDES

BY

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# PREPARATION AND CHARACTERIZATION OF SEVERAL CONDUCTING TRANSITION METAL OXIDES

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## ABSTRACT

The structure-property relationships of several conducting transition metal oxides, as well as their preparative methods, are presented in this paper. The importance of preparing homogeneous phases with precisely known stoichiometry is emphasized. A comparison is also made of the various techniques used to prepare both polycrystalline and single crystal samples. For transition metal oxides, the metallic properties are discussed either in terms of metal-metal distances which are short enough to result in metallic behavior, or in terms of the formation of a  $\pi^*$  conduction band resulting from covalent metal-oxygen interactions. Metallic behavior is observed when the conduction bands are populated with either electrons or holes. The concentration of these carriers can be affected by either cation or anion substitutions. The discussion in this presentation will be limited to the elements Re, Ti, V, Cr, Mo, and Cu.

## INTRODUCTION

It is not possible in this paper to discuss all of the known conducting oxides. This treatment will be limited to a number of binary and complex oxides which have been carefully prepared and characterized. It is hoped that the review of these representative conducting transition metal oxides will enable the reader to appreciate the importance of careful chemistry in the understanding of their properties. The structure and electronic properties of transition metal oxides depend on the stoichiometry and homogeneity of the prepared phases. Poorly prepared compounds cannot be effectively characterized. Consequently, an understanding of the variables which influence homogeneity and stoichiometry is important if progress is to be made in developing new oxides which are both of fundamental interest and useful for practical applications. In this paper the discussion will be limited to three structure types, namely  $\text{ReO}_3$ , rutile and  $\text{CuO}$ . The discussion of each structure type will be illustrated with specific compounds and will encompass problems encountered in their preparation and characterization. The relationship between structure, stoichiometry and conductivity will be emphasized, and correlations will be made in terms of the one-electron energy diagrams proposed and used so successfully by J. B. Goodenough.

### Rhenium(VI) Oxide

Biltz and his co-workers first reported the preparation of  $\text{ReO}_3$  [1,2]. Improved methods for its preparation were described by Nechankin et al. [3]. The oxide is red and reported to be diamagnetic [4]. Ferretti, Rogers and Goodenough [5] indicated that  $\text{ReO}_3$  exists with a considerable range of composition. Since the electrical properties are dependent on the sample stoichiometry, pure stoichiometric single crystals were grown by chemical vapor transport of  $\text{ReO}_3$  obtained by the reduction of  $\text{Re}_2\text{O}_7$  with  $\text{CO}$ . Non-stoichiometric  $\text{ReO}_3$  was produced by the reduction process, but purified when transported in a two-zone furnace with iodine as the transport agent. The transported, purified crystals were found to be stoichiometric within the limits of the analytical procedure used ( $\pm 0.2\%$ ) [6]. Resistivity measurements made on single crystals of stoichiometric  $\text{ReO}_3$  [5] indicated that they exhibited metallic behavior.

In the  $\text{ReO}_3$  structure (Fig. 1), the oxygen atoms occupy three-quarters of the positions in a cubic close-packed type lattice. The rhenium atoms occupy one-quarter of the available octahedral sites. The unit of structure, as represented in Fig. 1, is a simple cube of rhenium atoms with oxygen atoms on all of the twelve edge centers. The cubic  $\text{ReO}_3$  structure is the simplest three-dimensional structure formed from vertex sharing of octahedral ( $\text{ReO}_6$ ) groups. Each rhenium, therefore, has six oxygen nearest neighbors and each oxygen atom has two rhenium neighbors arranged linearly.

According to Morin [7] and Goodenough [8], for  $\text{ReO}_3$  where rhenium is in the +6 oxidation state, the crystal environment permits the formation of a conduction band by  $\pi$  overlapping of the metal "d" orbitals with the  $p_\pi$  orbital of the oxygen. For the  $\text{ReO}_3$  structure (Fig. 2), each anion contributes two  $\sigma$  orbitals ( $sp$ ) and two  $\pi$  orbitals  $p_\pi^2$ . Each octahedrally coordinated cation contributes six  $\sigma$  orbitals ( $e_g^2 sp^3$ ) and three  $\pi$  orbitals ( $t_{2g}^3$ ). A large overlap of the metal  $t_{2g}$  and anion  $p_\pi$  orbitals can result in the formation of bonding and antibonding  $\pi$  bands (Fig. 2) [8]. In Fig. 2, the  $\sigma$  and  $\pi$  bands are composed of bonding orbitals and the  $\sigma^*$  and  $\pi^*$  bands of antibonding orbitals. The  $p_\pi^*$  energy level is a non-bonding state and is composed of anion  $p_\pi$  orbitals. The number of states is designated by  $[n]$  and refers to the spin and orbital degeneracies per molecule.  $\text{ReO}_3$  has 25 outer electrons per molecule and hence can fill up to one-sixth of the total number of  $\pi^*$  states. Hence, this model is consistent with the observed metallic behavior of  $\text{ReO}_3$ .

This model was confirmed by Ferretti, Rogers and Goodenough [5] who compared the electrical conductivity of single crystals of  $\text{ReO}_3$  with that of sintered bars of polycrystalline  $\text{Sr}_2\text{MgReO}_6$ . The latter compound is an ordered perovskite and was first prepared by Longo and Ward [9]. In this compound, the rhenium and magnesium atoms are at the centers of oxygen octahedra which are linked by vertex sharing.  $\text{Sr}_2\text{MgReO}_6$  differs from  $\text{ReO}_3$  in that  $\text{Mg}^{2+}$  and  $\text{Re}^{6+}$  are in a nearly perfect ordered arrangement; the rhenium atoms cannot approach each other through oxygen more closely than about 7.6Å. However, in  $\text{ReO}_3$ , the Re atoms are about 3.8Å apart.

Ferretti et al. [5] carried out an investigation to distinguish between models for the conduction band involving either direct overlap of  $t_{2g}$  orbitals across the face diagonal of the unit cell or indirect overlap ( $\pi$  bonding) of the  $t_{2g}$  metal orbitals and the oxygen  $p_\pi$  orbital. The former model would allow both compounds to be metallic, but the latter predicts metallic behavior (delocalized d-electrons) for  $\text{ReO}_3$  and semiconducting behavior, at most, for  $\text{Sr}_2\text{MgReO}_6$ .  $\text{Sr}_2\text{MgReO}_6$  was found to be a semiconductor which is consistent with metal-oxygen-metal overlap. Rhenium trioxide single crystals were found to be metallic conductors with conductivities approaching that of metallic silver. The compound was found to be diamagnetic, indicating that the weak Pauli paramagnetic moment expected from the conduction electrons is insufficient to overcome the diamagnetism of the electrons in closed shells.

#### $\text{TiO}_2$ and Transition Metal Dioxides with the Rutile Structure

One of the polymorphs of  $\text{TiO}_2$ , rutile, crystallizes with the structure shown in Fig. 3 (space group  $P4_2/mnm$ ). The metal coordinates are:  $\text{Ti}(0,0,0)$ ,  $(1/2,1/2,1/2)$  and  $0;\pm(x,x,0)$ ,  $\pm(1/2+x,1/2-x,1/2)$ . As can be seen from Fig. 3, the structure consists of chains of  $\text{TiO}_6$  octahedra and each pair share opposite edges. Each titanium atom is surrounded octahedrally by six oxygen atoms, whereas each oxygen is surrounded by three titanium atoms arranged as corners of an equilateral triangle. The structure, therefore, has a 6:3 coordination.

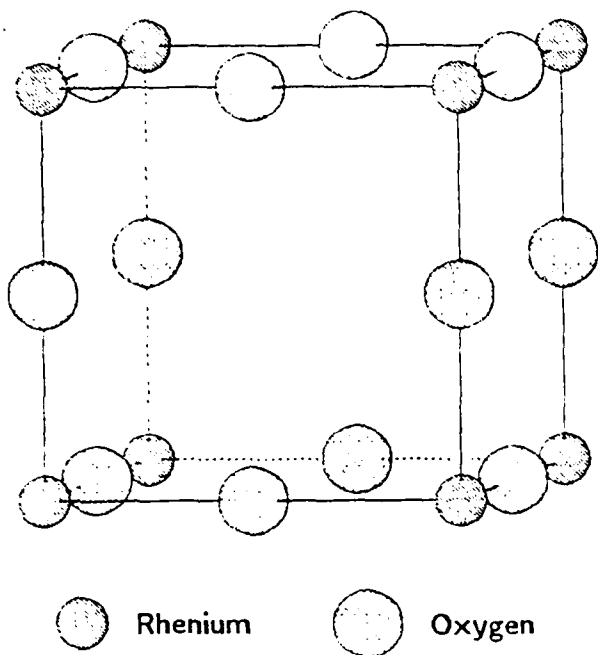


Fig. 1. Structure of  $\text{ReO}_3$

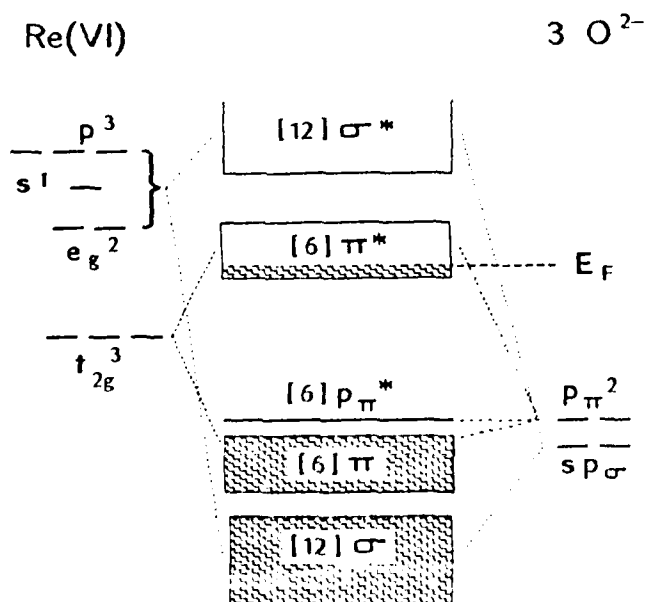


Fig. 2. Schematic Energy Bands for  $\text{ReO}_3$



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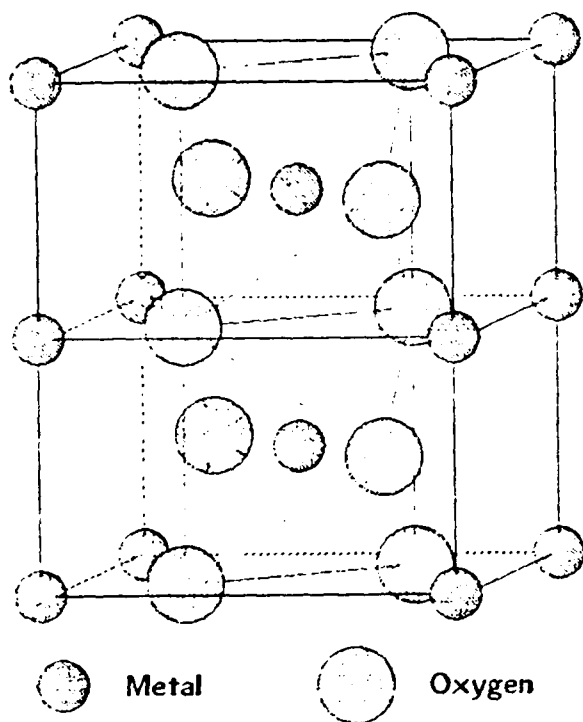


Fig. 3. Rutile Structure

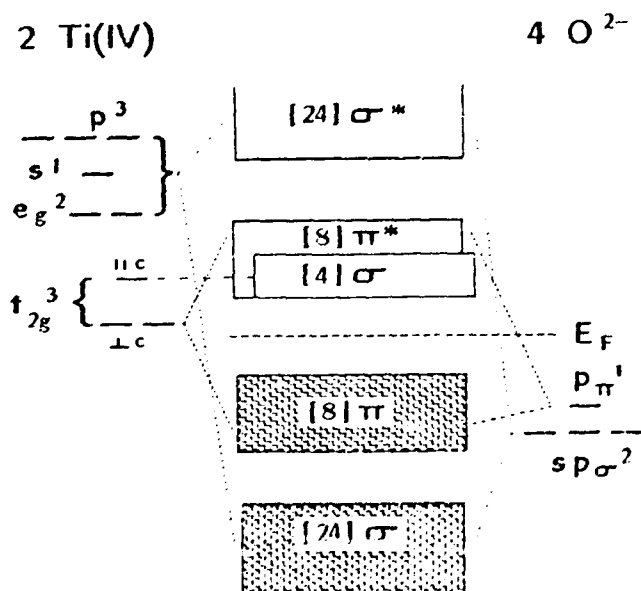


Fig. 4. Schematic Energy Bands for TiO<sub>2</sub>

A number of transition metal dioxides crystallize with rutile-related structures. Magnéli et al. [10-13], as well as Goodenough [8,14], have related certain properties of various transition metal dioxides to the number of transition metal d-electrons. Goodenough [8] has proposed, and Rogers [15] has applied, a one-electron energy diagram for  $\text{TiO}_2$  (rutile) and related compounds (Fig. 4). In this diagram the metal  $e_g^2sp^3$  wave functions of a doubled formula unit  $\text{Ti}_2\text{O}_4$  are mixed with hybridized  $sp^2$  wave functions of oxygen to form bonding and antibonding  $\sigma$  states. As a result of the long range ordering of the structure, the states are broadened to form bands with finite widths. Interaction between two  $t_{2g}$  cation orbitals ( $t_{2g\perp c}$ ) with the remaining oxygen  $p_\pi$  gives rise to bonding and antibonding  $\pi$  bands. The  $t_{2g\parallel c}$  orbitals of the cations are directed along the c axis and may form a  $\sigma$  band if the metal-metal separation is small enough for significant overlap to occur. The allowable number of electrons that can be accommodated by any band is given in brackets, and this number is equal to the product of the number of atoms per formula unit, the orbital degeneracy per atom and the spin degeneracy per atom. The rutile  $\text{TiO}_2$  has an electronic configuration of  $3d^0$  for Ti(IV). The Ti-O  $\sigma$  and  $\pi$  bands are completely filled so that the Fermi level is located at the middle of the energy gap between these bands and the antibonding  $\pi^*$  and cation-cation d-bands. Hence,  $\text{TiO}_2$  (rutile) should be a semiconductor and become metallic when the Fermi level is raised as the  $\text{TiO}_2$  is reduced to form some Ti(III)  $3d^1$  states.

#### Vanadium (IV) Oxides

The vanadium oxides with compositions between  $\text{V}_2\text{O}_3$  and  $\text{VO}_2$  are formed from slabs of a rutile-like structure sharing faces. Each of these phases shows transitions from the semiconducting to metallic state. Many of their properties can also be explained by considering structural changes which occur at the transition and utilizing the concepts of Goodenough [8] in which strong covalent mixing with oxygen  $p_\pi$  orbitals to form a  $\pi^*$  band plays a central role (Fig. 5a). For  $\text{VO}_2$ , above the transition temperature of  $67^\circ\text{C}$ , these bands overlap and are partially filled, giving rise to metallic conductivity. The compound is tetragonal ( $P4_2/mnm$ ) and all the V-V distances are equal (2.87Å). Below the transition temperature, the formation of V-V pairs along the tetragonal c-axis causes a doubling of the crystallographic unit cell [16], and a splitting of the  $t_{2g\parallel c}$  orbital in two (Fig. 5b). The resulting lower  $\sigma$  level lies below the bottom of the  $\pi^*$  band, becomes filled and lowers the Fermi energy below the bottom of the  $\pi^*$  band. The  $\pi^*$  band, arising from covalent mixing, is now empty [8]. Excitation of electrons from the filled  $\sigma$  level to the bottom of the  $\pi^*$  band gives rise to the semiconducting behavior.

#### Other Transition Metal Dioxides Crystallizing with the Rutile Structure

The simple model proposed by Goodenough [8,14] has been applied by Rogers [15] to account for the electronic behavior of the transition metal dioxides with rutile-like structures. Molybdenum(IV) oxide has 2 unpaired electrons for each molybdenum atom. Therefore, one electron is available for Mo-Mo  $\sigma$  bonding and the second electron can partially fill the Mo-O  $\pi^*$  band (Fig. 6). However, the short Mo-Mo separation is not fully consistent with a single  $\sigma$  bond. Hence, some of the electrons from the metal oxygen  $\pi$  band are promoted to a metal-metal  $\pi$  band which is located at the same energy level as the metal-metal  $\sigma$  state [15].

For  $\text{CrO}_2$ , Rogers [15] has indicated that there is a sharp decrease in direct cation-cation bonding. Hence, the  $t_{2g\parallel c}$  do not enter into metal-metal  $\sigma$  bonds, but remain at discrete cation sites in this compound (Fig. 7). The existence of these non-bonding sites within the  $\pi^*$  band is consistent with the

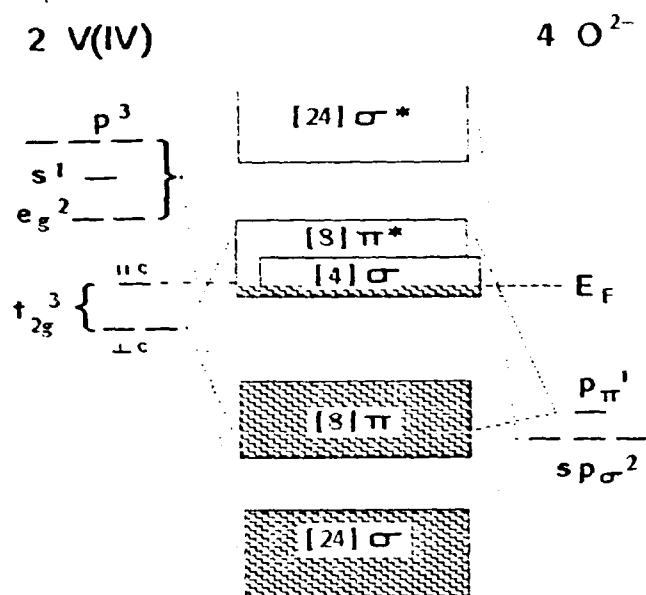


Fig. 5a. Schematic Energy Bands for Tetragonal VO<sub>2</sub>

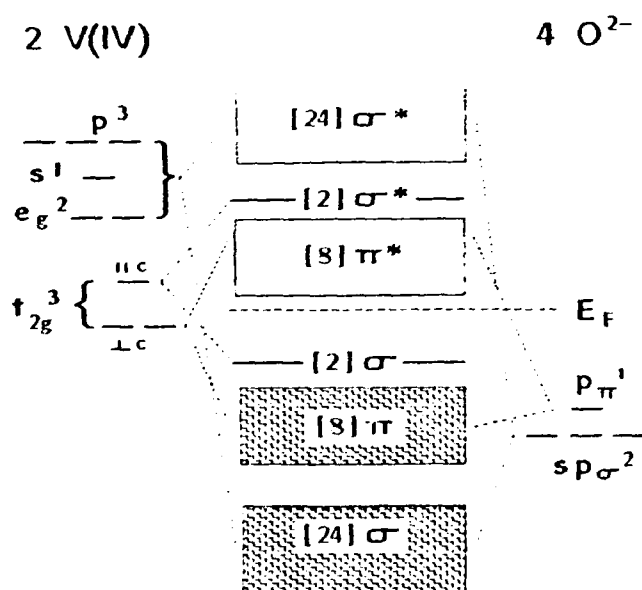


Fig. 5b. Schematic Energy Bands for Monoclinic VO<sub>2</sub>



2 Mo(IV)

4 O<sup>2-</sup>

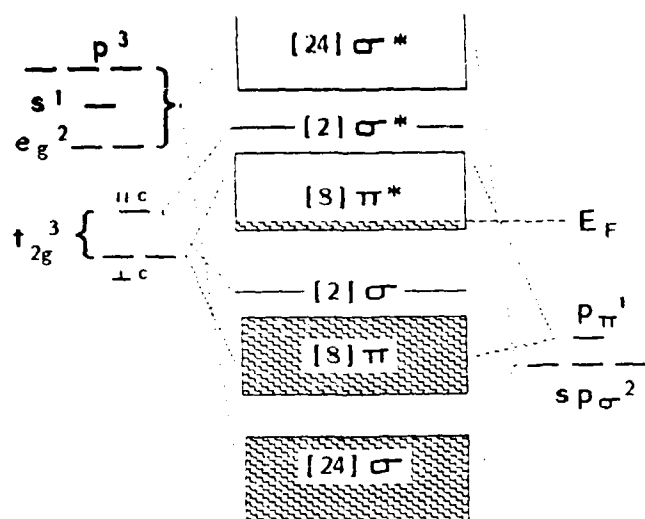


Fig. 6. Schematic Energy Bands for MoO<sub>3</sub>

2 Cr(IV)

4 O<sup>2-</sup>

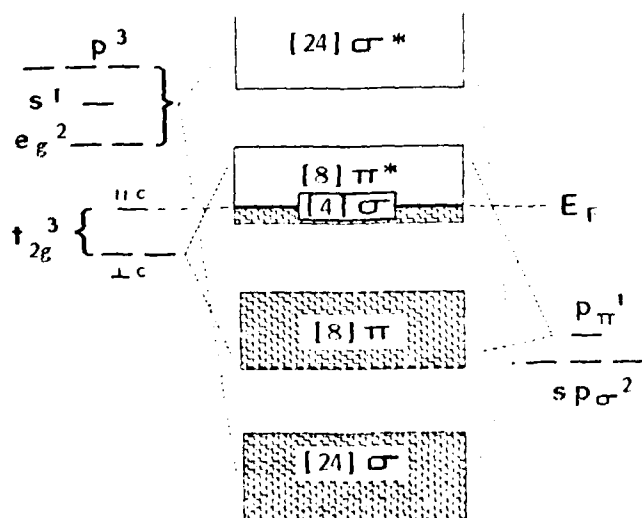


Fig. 7. Schematic Energy Bands for CrO<sub>2</sub>

observed ferromagnetic metallic properties of  $\text{CrO}_3$ . A number of the platinum metal dioxides, e.g. Ru, Ir, Os and possibly Rh, show metallic behavior which is consistent with the partial filling of the metal-oxygen  $\pi^*$  band. For  $\text{PtO}_2$  where the  $\pi^*$  band is filled, the Fermi level is raised to lie between the  $\pi^*$  and  $\sigma^*$  bands and the compound should behave as a semiconductor. Rogers [15] has reported powder samples of  $\text{PtO}_2$  to be semiconducting.

### Copper Oxides

Copper(II) oxide occurs in nature as the mineral tenorite. The structure [17] shows Cu(II) with square planar coordination of oxygen around the copper. The space group is  $C2/c$  with unit cell dimensions  $a = 4.6837(5)\text{\AA}$ ,  $b = 3.4226(5)\text{\AA}$ ,  $c = 5.1288(6)\text{\AA}$  and  $\beta = 99.54(1)^\circ$ . Fig. 8 shows the chains of oxygen coordination parallelograms formed by sharing edges. The structure is a distorted PdO type with two O-Cu-O angles of  $84.5^\circ$  and two of  $95.5^\circ$ . Each copper has 4 O' neighbors at  $1.96\text{\AA}$  and two next nearest O'' neighbors at  $2.78\text{\AA}$ . The line O''-Cu-O'' is inclined at  $17^\circ$  to the normal to the  $\text{Cu}(\text{O}')_4$  plane and the shortest Cu-Cu distance is  $2.90\text{\AA}$ .

Another oxide of copper,  $\text{Cu}_{16}\text{O}_{14}$  has been reported [18]. It is the rare mineral paramelaconite and crystallizes with the space group  $I4_1/amd$ , with unit cell dimensions  $a = 5.817\text{\AA}$ ,  $c = 9.803\text{\AA}$ . The structure is related to tenorite but the oxygen vacancies result in a rearrangement of the monoclinic tenorite structure to a tetragonal one.

In Cu(II) oxide, the Jahn-Teller distortion due to the stabilization of a single d-hole per atom,  $\text{Cu}(\text{II})3d^9$ , results in the observed difference of its structure with the monoxides of the other first row transition metals. For CuO, the equatorial oxygen  $p_\sigma$  overlaps strongly with the  $d_{(x^2-y^2)}$  orbital to form  $\sigma$  bands, but little, if any, with the  $d_{(z^2)}$ . The copper  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$  orbitals contribute to the formation of  $\pi$  bands. O'Keefe and Stone [19], Roden et al. [20], as well as Yang et al. [21], have indicated that CuO is antiferromagnetic with an observed anomaly in the magnetic susceptibility at 230 K. The Goodenough band model [22,23] indicates that when antiferromagnetic behavior is observed in the copper oxides, a separation may occur between the empty  $\sigma^*$  band states of the Cu(II/I) couple and the occupied  $\sigma^*$  band states of the Cu(III/II) couple. This is shown in Fig. 9 where the Fermi energy is placed near the top of the filled  $\pi^*$  band. The antiferromagnetic behavior of CuO is not typical, since the data reported by Roden [20] do not show a maximum of  $\chi$  at the antiferromagnetic ordering temperature. The unusual ordering can be related to the magnitude, or even existence, of the  $\sigma^*$  bandsplitting. In the case where Cu(III) is formed, the sign of the carrier results unambiguously from the formation of holes in the top of the  $\pi^*$  band. Where Cu(I) is formed, in addition to any electrons entering the  $\sigma^*$  (Cu(II/I) band, holes in the  $\pi^*$  band are also created by thermal excitation. Since the  $\sigma^*$  bands are narrow, the greater mobility of the holes in the  $\pi^*$  band will determine the sign of the dominant carrier. Koffeyberg [24] has indicated that CuO can only be prepared as p-type.

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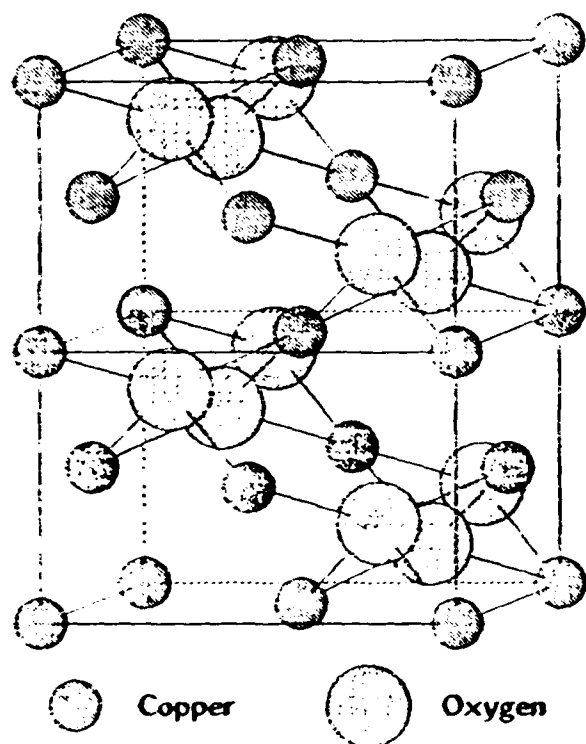


Fig. 8. Structure of CuO

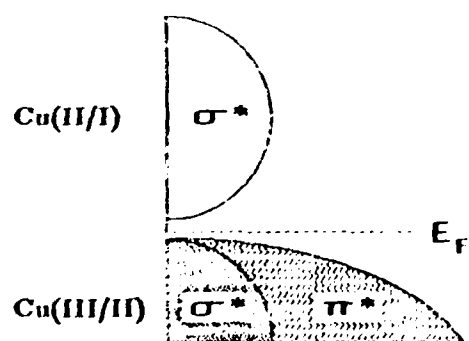


Fig. 9. Schematic Band Structure for CuO

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